

The Wettability of LaRC Colorless Polyimide Resins on Casting Surfaces

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INTRODUCTION

Two colorless polyimides developed at NASA Langley Research Center, LaRC™-CP1 and LaRC™-CP2, are noted for being optically transparent, resistant to radiation, and soluble in the imide form.¹⁻³ These materials may be used to make transparent, thin polymer films for building large space reflector/collector inflatable antennas, solar arrays, radiometers, etc. Structures such as these require large area, seamless films produced via spin casting or spray coating the soluble imide on a variety of substrates. The ability of the soluble imide to wet and spread over the mandrel or casting substrate is needed information for processing these structures with minimum waste and reprocessing, thereby, reducing the production costs.⁴ The wettability of a liquid is reported as the contact angle of the solid/liquid system.^{5,6} This fairly simple measurement is complicated by the porosity and the amount of contamination of the solid substrate.^{7,8} This work investigates the effect of inherent viscosity, concentration of polyimide solids, and solvent type on the wettability of various curing surfaces.

EXPERIMENTAL

Materials

The LaRC™-CP1 (2,2-bis(3-aminophenyl) hexafluoropropane +2,2-bis[4-(4-aminophenoxy) phenyl]hexafluoropropane) and the LaRC™-CP2 (2,2-bis(3-aminophenyl) hexafluoropropane + 1,3-bis(3-aminophenoxy)benzene) were obtained from IMITEC, Inc., Schenectady, NY.

The solvents, HPLC grade N,N-dimethylacetamid (DMAc) and 99.5%, anhydrous 2-methoxyethyl ether (diglyme) were obtained from Aldrich Chemical Company, Inc. Purum grade 1-methyl-2-pyrrolidone (NMP) was obtained from Fluka. Anhydrous ethyl alcohol (200-proof) was obtained from Pharmco Products, Inc.

The casting surfaces used for this study were soda lime glass, reflective aluminum sheet from Aluminum Company of America with a specular Alzak finish on one side, and a phenol resin substrate manufactured by SRS Technologies, Huntsville,

AL. One phenolic resin substrate was coated with Frekote 33 release agent.

Preparation of Polyimide Solutions

Various concentrations (w/w) of polyimide resins were prepared by dissolving the polyimide powder into the desired solvent and stirring the resin for 4-24 hours. The resins were then capped and stored in a freezer until needed for testing, at which time they were placed on a stirrer until they reached room temperature.

Preparation of Substrates

Prior to their initial use, and then after each use, the soda lime and aluminum substrates were wiped with ethyl alcohol using lint-free optical lens paper and the phenolic resin substrates were wiped with lint-free wipes. All substrates were then wrapped in lint-free wipes, and stored in a dessicator until measurements were made.

Contact Angle Measurements

The contact angle of the resins were measured using a remé-hart, inc. contact angle goniometer with a Dage-MTI, Inc. model 65, MK IV series camera, and a Javelin Electronics, Inc., model BWM9 monitor. A Canon video printer was used to record images of the drops. When possible, a microsyringe was used to measure out 5 μ L drops; for very viscous solutions, the needle was dipped into the solution and the resin coating the outside of the needle was dropped onto the substrate. The contact angle was measured on both sides of the drop and averaged for 5 drops. All measurements were made within 30 seconds of the drop formation.

RESULTS AND DISCUSSION

Three LaRCTM-CP1 imide powders of different molecular weights were selected for this research. Solutions of LaRCTM-CP1 and LaRCTM-CP2 were prepared in concentrations of 5, 10, 15, and 20 % solids in DMAc. Inherent viscosities (η_{INH}) were measured for each imide. The LaRCTM-CP2 had an inherent viscosity of 0.81 dL/g; the three LaRCTM-CP1 powders had η_{INH} of 0.64, 1.17, and 2.28 dL/g. The average contact angle of each solution on the various substrates are listed in table 1.

Generally, as the imide concentration increases, the average contact angle increases and the resin wetting decreases; also, the least wetting or the greatest contact angle occurs with the phenolic substrate with a release agent. One of the more interesting results of this research can be seen with the LaRCTM-CP1 data on the Al substrate; as the inherent viscosity of the imide increases, so does the average contact angle of the resin.

Looking at the series of 5% solids LaRC™-CP1 in DMAc of increasing η_{INH} , the contact angles increase from 15.6, to 21.6, and finally 22.3. This also occurs with the 10, 15, and 20% concentrations. This same trend is seen with these solution series with the other substrates; however, because of the porosity and surface imperfections of these substrates, the data has more scatter.

In an effort to reduce the error deviation, an investigation was performed on cleaning procedures for the soda lime glass. Alternate cleaning procedures investigated were: 1) cleaning in an ultrasonic cleaner with Allconox for 20 minutes, rinsing with deionized water, drying with lint-free wipes, and storing the plates in a dessicator; 2) cleaning in hot NaOH/ethanol solution, rinsing with deionized water, drying with lint-free wipes, and storing the plates in a dessicator, and 3) rubbing with optical lens paper saturated with ethanol, air drying, and storing the plates in a dessicator. The cleaning procedure reported in the experimental section above proved to be equal to or better than any of cleaning procedures investigated for reproducing data.

Solutions of LaRC™-CP1 ($\eta_{INH} = 1.17$ dL/g) were made in diglyme and NMP; the contact angles for concentrations of 5, 10, and 15 % solids are reported in tables 2 and 3 (the solutions of 20% solids were too thick for accurate measurements). The trend of increased average contact angle with increase imide concentration is not obvious for this series of resins as with the resins series in DMAc. For the diglyme and NMP sets of solutions, similar wetting occurred for all concentrations on all substances. The decreased dependence of contact angle on polymer concentration and on substrate surface when using diglyme and NMP could neatly simplify spin casting or spray coating from these solvents.

Acknowledgements

The author would like to thank Lois A. Forbes, Engineering Technician, Operations Support Division, NASA Langley Research Center for researching and acquiring the optical equipment necessary for this work and for setting up the contact angle goniometer apparatus.

CONCLUSIONS

The wetting of casting substrates by LaRC™-CP1 polyimide resin decreased with increased polymer inherent viscosity and increased imide concentration in DMAc. The trend of decreased wettability for increased imide concentration was not observed for the polyimide in diglyme or NMP. These results are useful for spin casting and spray coating the soluble imide over mandrels and casting surfaces necessary for making the large area, seamless films used for space antennas, arrays, and radiometers.

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Table 1
Contact Angles of Resins in DMAc

Average Contact Angle (°)					
Resin System	% Solids	Glass	Al	Phenolic	Ph w/RA *
DMAc	0	10.9 ±0.8	15.9 ±1.3	27.5 ±1.4	46.1 ±0.5
LaRC™-CP2	5	11.6 ±2.0	12.5 ±1.7	23.0 ±1.0	52.3 ±0.8
(0.81)**	10	24.2 ±4.9	13.9 ±1.0	29.2 ±1.5	58.0 ±1.2
	15	26.0 ±2.9	15.5 ±1.0	31.2 ±2.4	56.6 ±0.7
	20	32.8 ±2.0	28.5 ±4.5	31.8 ±2.1	44.4 ±1.2
LaRC™-CP1	5	12.4 ±2.6	15.6 ±0.8	26.3 ±1.4	53.1 ±0.2
(0.64)**	10	15.8 ±2.9	19.1 ±4.2	22.2 ±2.5	54.3 ±0.8
	15	18.1 ±1.1	19.6 ±1.0	22.8 ±3.7	36.3 ±0.1
	20	24.2 ±1.0	26.9 ±1.0	28.8 ±2.3	39.0 ±3.3
LaRC™-CP1	5	6.5 ±2.4	21.6 ±1.9	22.8 ±1.7	46.9 ±1.1
(1.17)**	10	11.3 ±1.2	21.2 ±1.2	17.6 ±1.9	52.1 ±1.0
	15	16.5 ±0.9	24.6 ±2.8	30.2 ±4.0	52.7 ±1.0
	20	37.6 ±4.9	44.8 ±2.5	45.7 ±4.5	68.6 ±1.4
LaRC™-CP1	5	14.3 ±0.8	22.3 ±2.5	18.9 ±0.8	52.2 ±0.5
(2.28)**	10	31.8 ±1.9	33.1 ±1.5	34.6 ±3.7	62.5 ±0.5
	15	54.6 ±4.9	62.7 ±3.6	59.2 ±3.0	71.2 ±1.3
	20	gel	gel	gel	gel

* Phenolic resin substrate with Frekote 33 release agent.

** Inherent Viscosity (dL/g)

Table 2
Contact Angles of LaRC™-CP1 ($\eta_{INH} = 1.17$ dL/g) in Diglyme

Average Contact Angle (°)				
% Solids	Glass	Al	Phenolic	Ph w/RA*
0	15.0 ±1.8	2.5 ±1.1	0	16.3 ±1.3
5	23.7 ±1.7	28.8 ±1.8	26.8 ±2.8	32.7 ±1.9
10	27.0 ±2.8	31.1 ±2.0	30.6 ±2.3	27.0 ±0.5
15	28.6 ±3.0	30.7 ±0.8	23.4 ±1.4	39.2 ±2.0

* Phenolic resin substrate with Frekote 33 release agent.

Table 3
Contact Angles of LaRC™-CP1 ($\eta_{INH} = 1.17$ dL/g) in NMP

Average Contact Angle (°)				
% Solids	Glass	Al	Phenolic	Ph w/RA*
0	14.8 ±2.6	28.8 ±1.4	16.6 ±1.8	30.6 ±0.6
5	26.7 ±1.7	14.6 ±1.5	12.8 ±0.8	17.2 ±0.0
10	25.4 ±1.2	22.9 ±1.6	24.0 ±1.6	25.0 ±1.9
15	39.8 ±1.6	35.2 ±1.6	38.5 ±2.2	34.4 ±0.9

* Phenolic resin substrate with Frekote 33 release agent.